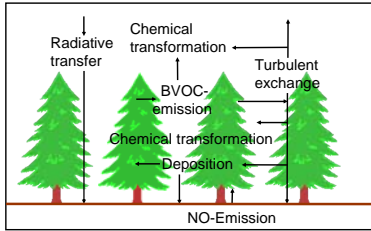


# A Model to Describe Chemical Transformations of Biogenic VOC and Canopy Fluxes: A Contribution to Improve the Quantification of Biogenic VOC Emissions

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## Problem



BVOC emission of forests is a result of primary emission from soil, trunk and crown sources modified by deposition as well as chemical transformation processes. This net emission is needed for assessing the impact of forest emissions on regional air quality.

However, current forest net BVOC emission estimates are rather crude by neglecting the complex interaction and feedback loops of processes involved.

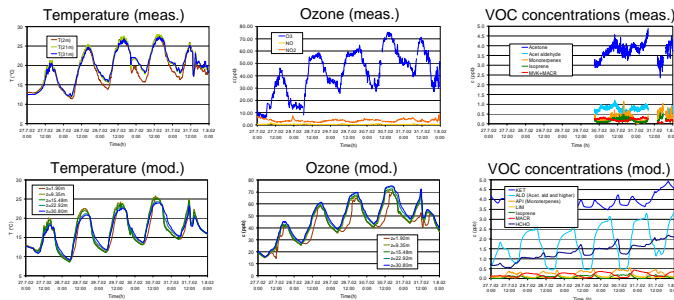
## Solution

Numerical modelling is an efficient tool to investigate the role of chemical degradation of BVOC and the effect of dynamical processes on BVOC and product concentrations within and above the canopy. Starting from specified initial conditions the one-dimensional canopy-chemistry model CACHE (Canopy Atmospheric CHEmistry Emission model, Forkel et al. 2001) predicts profiles of temperature, humidity, and chemical species. CACHE includes the energy balance at the leaf surfaces, turbulent transport of heat, water vapour, and gas phase chemical compounds within and above the canopy, heat and moisture transport in the soil, emission of biogenic VOC, chemical transformation, and deposition. Chemical transformations are usually computed with the RACM gas phase chemistry mechanism of Stockwell et al. (1997). Additionally, a RACM with updated isoprene chemistry is available.

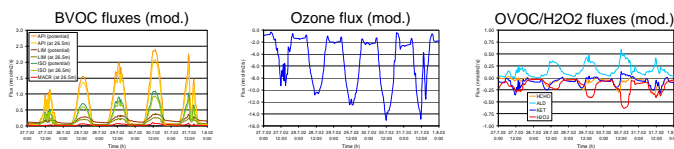
## Results

### Simulation of 'Golden Days' and model validation

The extensive BEWA2000 field measurements within a 20 m high spruce forest at the Waldstein site offer the possibility to compare the model results with a complete set of observations.



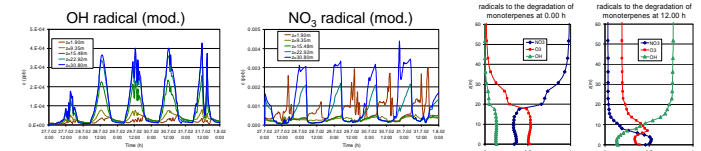
The simulated course of temperature and ozone shows good agreement with the measurements at the Waldstein site. The modeled course of isoprene, monoterpenes, and ketones reproduce the measured diurnal course with maximum values in the morning and evening hours, which is due to the changing magnitudes of emission, chemical transformation, turbulent exchange, and deposition during the course of the day.



The measured fluxes of isoprene and monoterpenes are well reproduced by the simulations. Chemical reactions lead to 10 to 20% lower BVOC fluxes above the canopy as compared to the potential fluxes. The modeled nocturnal ozone flux towards the canopy was found to be one main reason for the nocturnal drop of the ozone concentration. Modeled daytime ozone fluxes showed fair agreement with the measurements.

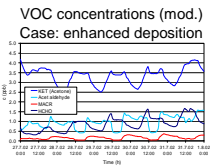
### Radical concentrations

The importance of the nighttime NO<sub>3</sub> reaction with monoterpenes could be demonstrated by the measurements at the Waldstein site. The model results show pronounced differences between the radical concentrations within and above the canopy. Furthermore, the simulations indicate that within the dense forest canopy the NO<sub>3</sub> radical can also contribute to the monoterpene oxidation during the daylight hours.

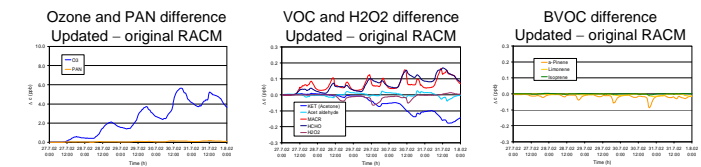


### Sensitivity studies

Little is known about the deposition of the products of BVOC chemistry. Recent findings indicate that the deposition velocities of oxidized compounds may be underestimated. As compared to the base case (shown at the left side) the accumulation of aldehydes during the nighttime is reduced significantly when a higher transfer through the mesophyll is assumed.



The knowledge about details of the isoprene oxidation has increased significantly during the last years. Therefore, RACM with an updated isoprene degradation mechanism, which was adapted from the joint project ValCheM, (Geiger et al, 2003) was implemented into CACHE. As compared with the ozone concentrations computed with the original RACM (shown on the left side) the new mechanism yields up to 8% higher ozone and also slightly different VOC concentrations.



## Summary

- Simulations with the canopy-chemistry model CACHE have shown that
- Chemical degradation within the forest reduces the BVOC fluxes by about 10 to 20% as compared to the potential fluxes
- Deposition plays a major role for the balance of the oxidation products of biogenic VOCs
- Within the dense forest canopy the NO<sub>3</sub> radical can also contribute to the monoterpene oxidation during the daylight hours
- The application of an updated description of the isoprene chemistry in the RACM mechanism results in higher simulated ozone and MACR (methacrolein+MVK) concentrations for the regarded conditions.

## Conclusion

The one-dimensional canopy-chemistry model CACHE was applied to the 21 'Golden Days' and some additional days of the BEWA 2000 field campaigns at the Waldstein. The results of the simulations indicate that the model is generally able to reproduce the observed features and can be used as a tool for process studies.

### References

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Geiger, H. I. Barnes, I. Benjan, Th. Benter, M. Spittler, 2003: The tropospheric degradation of isoprene: an updated module for the regional atmospheric chemistry mechanism. Atmospheric Environment 37, 1503-1519.

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